Studies on Determinations of Metals by Extraction Method of Metal Organic Compound. IV : Determinations of Cadmium and Arsenic with Sodium Diethyldithiocarbamate

Studies on Determinations of Metals by Extraction Method of Metal Organic Compound. IV

Determinations of Cadmium and Arsenic with Sodium Diethyldithiocarbamate*

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Synopsis

Cadmium and arsenic form white precipitate or turbidity with sodium diethyl-dithiocarbamate, and the precipitate or the turbidity was extracted completely with some organic solvents and gives clear extracts, and the transmittancy was measured successfully with Beckman model DU spectrophotometer at a suitable wave length. Cadmium complex with the reagent was extracted completely from the solution at from 2N of hydrochloric acid to pH 9.5 by carbon tetrachloride, chloroform, benzene, toluene and xylene. Trivalent arsenic complex was extracted completely from the solution at pH 3~6 with these solvents.

The most suitable absorbancy of the cadmium complex was given at the wave length of 440 mμ of the Beckman model DU spectrophotometer and that of the trivant arsenic complex was given at 340 mμ. From the linear relations of the extinctancy of the extract measured at the suitable wave length against the metal content, cadmium as small as 20γ and trivalent arsenic as small as 5γ were determined.

I. Introduction

Cadmium and arsenic react upon sodium diethyl-dithiocarbamate and form white precipitate or turbidity as lead, silver and mercury do[1], and the precipitate or the turbidity is also extractable with some organic solvents and each gives transparent extract. The behaviour have been used only for a separation of cadmium in its microdetermination by Chernikhov and Dobnikina[2], and that of arsenic have been reported only qualitatively. As the extracts had not been utiliped directly for the determinations of these metals, the present experiments were carried out by means of the Beckman model DU spectrophotometer in order to make clear the relation of the extinctancy of extracts against the metal content, a suitable extracting solvent, a suitable pH range of the solution for the extraction and the determinable amounts of these metals.

II. Experimental results

(1) Instrument and method for the measurement

All are the same as in the 3rd report[1].

Reagent

Cadmium standard solution (200 γ/ml) was prepared from cadmium nitrate of

* The 747th report of the Research Institute for Iron, Steel and Other Metals.
Published in the Journal of the Chemical Society of Japan, **73** (1952), 693.

(1) J. Chem. Soc. Japan, **73** (1952), 626.
(2) Y. A. Chernikhov and B. M. Dolkina, Zavodskaya Lab., **15** (1949), 906.

"extra pure" grade and standarized gravimetrically by "oxine" method; arsenic standard solutions (100 γ/ml) were prepared from "Kahlbaum" arsenous oxide. Other reagents were all the same as in the 3rd report[1].

(2) Absorbancy curve

Absorbancy curves were drawn by the transmittancy of the extracts obtained at 320~1000 mμ by the extractions with carbon tetrachloride of cadmium and trivalent arsenic complexes with sodium diethyl-dithiocarbamate.

Experimental procedure

Taking 1 ml of each metal standard solution and 10 ml of the buffer solution of pH 5, 2 ml of 2 per cent sodium diethyl-dithiocarbamate solution and 5 ml of carbon tetrachloride were added in a separatory funnel, and it was shaken vigorously for one minute. After it was settled, the carbon tetrachloride layer was drawn off from the aqueous layer and the transmittancy of the extracts was measured in a 1 cm cell at the wave length 320~1000 mμ.

The Blanks runs was carried out by treating in the same way as the solution without only the metal. The absorbancy curves of cadmium and trivalent arsenic obtained are shown in Fig. 1. As shown in Fig. 1, the wave length of 440 mμ was most suitable for the estimation of cadmium and 340 mμ for that of arsenic, and the absorption of the reagent itself became very large with the lowering of ultraviolet range.

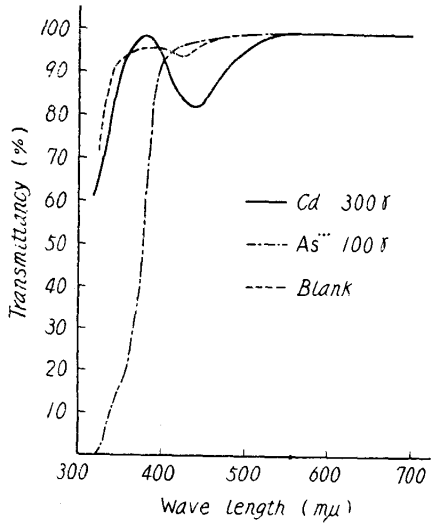

Fig. 1

(3) Influence of pH

Preparing various kinds of buffer solutions with various pH, the most suitable range of pH for the extraction was examined. Carbon tetrachloride was used as the extracting solvent, and the measurements were carried out with the wave length 440 mμ in the case of cadmium and 340 mμ in the case of arsenic. The results are shown in Fig. 2. As shown in Fig. 2, cadmium was completely extracted at lower than pH 9.5, but hardly at pH 10, and an acidity stronger than 2N of hydrochloric acid gave rather higher results. Trivalent arsenic was extracted at pH 3~6, but lower results were given at lower than pH 3 and no white turbidity with sodium diethyl-dithiocarbamate was formed at higher than pH 6.5. On the other hand, even if the arsenic content was 200 γ the hexavalent one formed no precipitate with sodium diethyl-dithiocarbamate

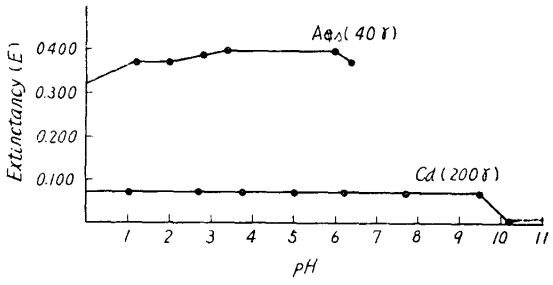

Fig. 2

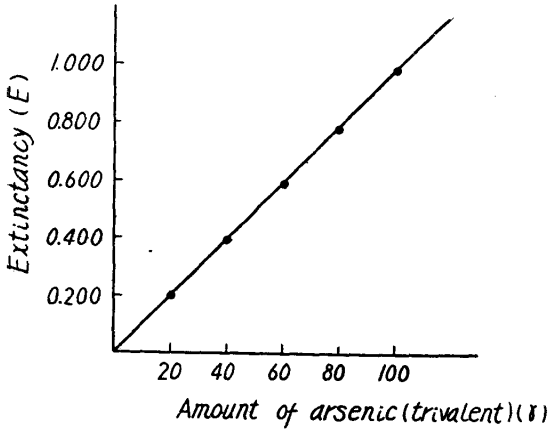

Fig. 3

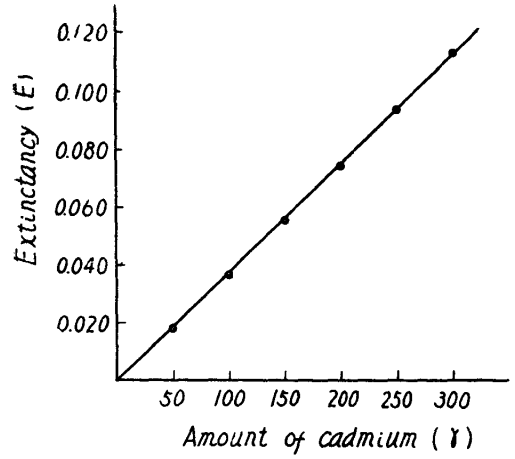

Fig. 4

solution and nothing was extracted.

(4) Relation between the amount of metal and extinctancy

Varying the metal content in solutions at pH 5 the extinctancy was measured. The results obtained gave two linear relations as shown in Fig. 3 and Fig. 4. It was found that 20~300γ of cadmium and 5~100γ of trivalent arsenic were determinable by the procedure.

(5) Solvents

Varying the extracting solvents, the extractabilities were compared with one another.

(i) Cadmiun

After extracting with 5 ml of each of carbon tetrachloride, benzene, toluene, xylene, chloroform, amylacetate and amylalcohol, the extinctancy was measured. The results were shown in Table 1. As shown in Table 1, benzene, toluene, xylene and chloroform gave much the same value as carbon tetrachloaide, but amylacetate and amylalcohol gave a little turbidity. 300γ of the cadmium content in the solution also was extracted completely by a single extraction with 5 ml of it and no absorption was found in the second extract.

Table 1

Solvents	Extinctancy (E)		
	Amount of Cadmium (γ)		
	100	200	300
Carbon tetrachloride	0.037	0.075	0.113
Benzene	0.036	0.076	0.113
Toluene	0.037	0.076	0.114
Xylene	0.035	0.073	0.110
Chloroform	0.035	0.074	0.111
Amylacetate		turbidity	
Amylalcohol		turbidity	

440 mμ pH 3.7

(ii) Arsenic

The extractions were carried out with these solvents. The results are shown in Table 2. As shown in Table 2, no distinguishable difference was found among

them, but carbon tetrachloride was the best, and chloroform, benzene, toluene and xylene gave similar, though rather lower, results. Amylacetate had a tendency to form a turbidity and the extract with amylalcohol showed almost no absorption.

Table 2

Solvents	Extinctancy (E)		
	Amount of Arsenic (trivalent) (γ)		
	20	60	100
Carbon tetrachloride	0.197	0.600	0.960
Chloroform	0.197	0.594	0.950
Benzene	0.180	0.540	0.923
Toluene	0.181	0.535	0.920
Xylene	0.180	0.540	0.920
Amylacetate		turbidity	

340 mμ pH 3.7

III. Consideration

Sach metals as give some colored extracts, were determined by the extraction method with organic solvents of the metals and sodium diethyl-dithiocarbamate complexes, but for lead, silver, mercury and cadmium, which give white turbidities giving clear extract with organic solvents, the extraction method has been used only for the separation of these metals and any further application to the determinations of them has not been reported yet. In the 3rd reports, lead, silver and mercury were discussed and so in the present, cadmium and arsenic were studied.

Chernikhov and Dobkina[2] reported only that cadmium was extractable at pH 3 with ethylacetate and could be separated by extracting with carbon tetrachloride and ethylacetate. R. L. Lacoste, M. H. Earing and S. E. Wirerley[3] reported only that both trivalent and hexavalent arsenic did not form any precipitate with sodium diethy-dithiocarbamate salt at pH of 3.7, 7.2 and 9.5. No other report concerning the subject was known. According to the present author's experiment, however, trivalent arsenic formed a white precipitate with sodium diethyl-dithiocarbamate at pH lower than 6.4, but not at higher pH, and hexavalent arsenic as much as about 200 γ did not entirely even in an acidic solution. Furthermore, linearities of extinctancy of the extracte of cadmium and trivalent arsenic complexes with sodium diethyl-dithiocarbamate were confirmed using several kinds of organic solvents against the metal amount and the suitable wave length for the extinctancy measurements, the suitable pH range for the extraction and the minimum content of the metals determinable by the procedure were found. It was concluded that cadmium and arsenic also were determinable directly by the extraction method with their sodium diethyl-dithiocarbamate complexes using organic solvents.

(3) R. L. Lacoste, M. H. Earing and S. E. Wiberley, Anal. Chem., **23** (1951), 871.

Summary

(1) Cadmium and trivalent arsenic formed a white precipitate or turbidity with sodium diethyl-dithiocarbamate, which were clearly soluble in organic solvents.

(2) According to the extinctancy curves obtained by means of Beckman model DU spectrophotometer, the most suitable wave lengths for the estimations were 440 mμ for cadmium and 340 mμ for arsenic.

(3) The extinctancy measured at the suitable wave length was linear against the metal content, and so cadmium as small as 20γ and trivalent arsenic as small as 5γ were determined by the procedure.

(4) Excepting amylalcohol and amylacetate, carbon tetrachloride, chloroform, benzene, toluene and xylene were all useful as an extracting solvent.

(5) The extraction of cadmium was carried out completely at the range of from 2N of hydrochloric acid solution to pH 9.5, and that of trivalent arsenic was also done at the pH range from 3 to 6. At pH larger than 6.5 the latter formed no white precipitate with sodium diethyl-dithiocarbamate and could not be extracted.

Acknoledgement

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